REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
26-01-2015	Final Report	1-Oct-2009 - 30-Sep-2013

4. TITLE AND SUBTITLE
Final Report: Nonlinear Analysis of Experimental Measurements 7.6. Theoretical Chemistry

5a. CONTRACT NUMBER
W911NF-09-1-0480

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
611102

6. AUTHORS
Jianshu Cao and late Robert Silbey

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
Massachusetts Institute of Technology (MIT
77 Massachusetts Ave

Cambridge, MA 02139 -4307

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
54523-CH.33

12. DISTRIBUTION AVAILIBILITY STATEMENT
Approved for Public Release; Distribution Unlimited

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT
During the period of ARO support, we worked on four projects: (a) generalized Michaelis-Menten equation for enzymatic reactions; (b) counting statistics of single molecule reaction trajectories and single cell microarray data (c) analysis of cytoadhesion and binding kinetics experiments; and (d) optimization of coherent energy transfer in photosynthetic light-harvesting systems. The results are summarized in several publications and manuscripts. These research projects are motivated by single molecule measurements of complex biophysical processes, including photosynthetic energy transfer, enzymatic turnover reactions, and adhesion of cells. Single molecule

15. SUBJECT TERMS
single molecule enzymatic networks, light-harvesting energy transfer, single molecule counting statistics, single cell measurements

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Robert Silbey
UU	UU	UU	UU		19b. TELEPHONE NUMBER 617-253-1470

Report Title

Final Report: Nonlinear Analysis of Experimental Measurements 7.6. Theoretical Chemistry

ABSTRACT

During the period of ARO support, we worked on four projects: (a) generalized Michaelis-Menten equation for enzymatic reactions; (b) counting statistics of single molecule reaction trajectories and single cell microarray data (c) analysis of cytoadhesion and binding kinetics experiments; and (d) optimization of coherent energy transfer in photosynthetic light-harvesting systems. The results are summarized in several publications and manuscripts. These research projects are motivated by single molecule measurements of complex biophysical processes, including photosynthetic energy transfer, enzymatic turnover reactions, and adhesion of cells. Single molecule experiments probe stochastic fluctuations on a broad range of temporal and spatial scales and therefore require detailed dynamic modeling and data analysis to extract useful molecular-level information. The sponsored research projects converge to a unified approach of correlating non-linear measurements with physical properties of complex systems.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
11/08/2011	1.00	Seongeun Yang, Jianshu Cao, Robert J. Silbey, Jaeyoung Sung. Quantitative Interpretation of the Randomness in Single Enzyme Turnover Times, Biophysical Journal, (8 2011): 519. doi: 10.1016/j.bpj.2011.06.022
11/08/2011	2.00	Jianshu Cao, Artem Efremov. Bistability of Cell Adhesion in Shear Flow, Biophysical Journal, (9 2011): 1032. doi: 10.1016/j.bpj.2011.07.026
11/08/2011	3.00	Jianshu Cao. Michaelis-Menten Equation and Detailed Balance in Enzymatic Networks, The Journal of Physical Chemistry B, (05 2011): 0. doi: 10.1021/jp110924w
12/18/2012	8.00	Wei Zhao, Justin Dauwels, Jacquin C Niles, Jianshu Cao. Computational synchronization of microarray data with application to Plasmodium falciparum, PROTEOMe science, (10 2012): 1. doi:
12/18/2012	10.00	Yu Rim Lim, Seong Jun Park, Bo Jung Park, Jianshu Cao, Robert J. Silbey, Jaeyoung Sung. Reaction Event Counting Statistics of Biopolymer Reaction Systems with Dynamic Heterogeneity, Journal of Chemical Theory and Computation, (04 2012): 0. doi: 10.1021/ct200785q
TOTAL:	**5**	

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received	Paper
01/26/2015 14.00	X. L. Xu, , H. Ge, , C. Gu, , Y. Q. Gao, , S. S. Wang, , B. J. R. Thio, , J. T. Hynes, , X. S. Xie, , J. Cao. Modeling Spatial Correlation of DNA Deformation: DNA Allostery in Protein Binding., J. Phys. B: At. Mol. Opt. Phys. , (06 2013): 13378. doi:
01/26/2015 12.00	Jianshu Cao, Jeremy Moix. A hybrid stochastic hierarchy equations of motion approach to treat the low temperature dynamics of non-Markovian open quantum systems., J. Chem Phys., (10 2013): 134106. doi:
01/26/2015 13.00	Liam Cleary, Jianshu Cao. Optimal thermal bath for robust excitation energy transfer in disordered light-harvesting complex 2 of purple bacteria., New Journal of Physics, (12 2013): 125030. doi:
01/26/2015 15.00	J. Cao, J. Moix. Coherent quantum transport in disordered systems: I. The influence of dephasing on the transport properties and absorption spectra on one-dimensional systems., New Journal of Physics, (08 2013): 85010. doi:
01/26/2015 16.00	J. Cao, N. A. Sinitsyn, S. Chaudhury. Universality of Poisson Indicator and Fano Factor of Transport Event Statistics in Ion Channels and Enzyme Kinetics., J. Phys. B: At. Mol. Opt. Phys. , (12 2012): 503. doi:
01/26/2015 17.00	H. Chen, C. Chuang, R. J. Silbey, J. Cao, L. Cleary. Optimal fold symmetry of LH2 rings on a photosynthetic membrane, PNAS, (03 2013): 8537. doi:
01/26/2015 18.00	J. Wu, R. Silbey, J. Cao. Generic Mechanism of Optimal Energy Transfer Efficiency: A Scaling Theory of the Mean First-Passage Time in Exciton Systems. , Phys Rev Lett, (05 2013): 200402. doi:
01/26/2015 19.00	X. Xu, A. K. Efremov, A. Li, M. Dao, C. T. Lim, J. Cao,. Probing the cytoadherence of malaria infected red blood cells under flow., PLoS ONE, (05 2013): 1. doi:
01/26/2015 20.00	X. Chen, J. Cao, R. Silbey. A Novel Construction of Complex-valued Gaussian Processes with Arbitrary Spectral Densities and its Application to Excitation Energy Transfer, J. Chem. Phys., (06 2013): 224104. doi:
01/26/2015 21.00	J. Wu, J. Cao. Higher-order kinetic expansion of quantum dissipative dynamics,: Mapping quantum networks to kinetic networks. , J. Chem. Phys., (07 2013): 44102. doi:
01/26/2015 22.00	J. X. Zhu, Y. Q. Ma, J. Cao, J. X. Chen. Translocation of a forced polymer chain through a crowded channel., Europhysics Letters, (04 2014): 18003. doi:
01/26/2015 23.00	J. X. Chen, J. X. Zhu, Y. Q. Ma, J. Cao. Translocation of a forced polymer chain through a crowded channel., Europhysics Letters, (04 2014): 18003. doi:
01/26/2015 24.00	X. L. Xu, B. J. R. Thio, J. Cao. Correlated Local Bending of a DNA Double Helix and Its Effect on DNA Flexibility in the Sub-Persistence-Length Regime., J. Phys. Chem. Lett., (08 2014): 2868. doi:

01/26/2015 25.00 L. Lai, J. Cao. Spectrins in axonal cytoskeletons: Dynamics revealed by extensions and fluctuations., J. Chem. Phys., (07 2014): 15101. doi:

01/26/2015 26.00 C. Chuang, J. Cao, C. Chen, V. Ball , D. Ruch, M. J. Buehler. Excitonic effects from geometric order and disorder explain broadband optical absorption in eumelanin, Nat. Commun., (05 2014): 3859. doi:

01/26/2015 27.00 S. Mehraeen, K. T. P. Lim, F. Wang, J. Cao, M. C. Tan, J. K. W. Yang, M. Asbahi. Template-Induced Structure Transition in Sub-10 nm Self-Assembling Nanoparticles, Nano Letters, (04 2014): 2642. doi:

01/26/2015 29.00 C. Wang, J. Ren, J. Cao. Optimal tunneling enhances the quantum photovoltaic effect in double quantum dots, New Journal of Physics, (04 2014): 45019. doi:

01/26/2015 30.00 X. Zhong, Y. Zhao, J. Cao. Coherent quantum transport in disordered systems: II. Temperature dependence of carrier diffusion coefficients from the time-dependent wavepacket diffusion method., New Journal of Physics, (04 2014): 45009. doi:

01/26/2015 31.00 J. Cerrillo, J. Cao. Non-Markovian Dynamical Maps: Numerical Processing of Open Quantum Trajectories, Phys. Rev. Lett., (03 2014): 110401. doi:

01/26/2015 32.00 W. Mu, J. Cao, Z. Ou-Yang. Shape transition of unstrained flattest single-walled carbon nanotubes under pressure, J. Appl. Phys., (01 2014): 44512. doi:

TOTAL: 20

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Robert Silbey: Energy Transfer, Coherence and Decoherence in Molecular Aggregates, invited paper, Gordon Conference on Electronic Processes In Organic Materials July 25-30, 2010, Mount Holyoke College, South Hadley, MA

Jianlan Wu: poster presentation, Gordon Conference on Electronic Processes In Organic Materials July 25-30, 2010, Mount Holyoke College, South Hadley, MA

Jianshu Cao: Optimal efficiency in light-harvesting energy transfer
CECAM workshop Workshop, on Coherent Quantum Dynamics in Complex Many-Body Systems, UDC, Dublin, May 9-12, 2010, invited talk

Jianshu Cao: Optimal efficiency in light-harvesting energy transfer
Canadian Society for Chemistry (CSC) Symposium, Coherence and decoherence in molecular processes,Toronto, May 29-June 2, 2010, invited talk

Jianshu Cao: Optimal efficiency in light-harvesting energy transfer, Workshop on Quantum effects in biological systems, Harvard, June 17-20, 2010, invited talk

Jianshu Cao: 'Selected topics on quantum dynamics', Summer School of Theoretical and Computational Chemistry, Beijing Normal University, Beijing, July 26-Aug 5, 2010, invited lectures

Jianshu Cao: 'Optimization of energy transfer processes in photosynthetic systems', ACS symposium 'Molecular Models for Solar Energy Conversion and Storage', Boston, Aug. 22-26, 2010, invited talk

Jianshu Cao: 'Signatures of quantum coherence in vibrational dynamics and energy transfer', ACS symposium 'Frontiers of Condensed Phase Theory and Simulation: A Tribute to Bruce J. Berne', Boston, Aug. 22-26, 2010, invited talk

Robert Silbey: 'Coherent Forster energy transfer in light-harvesting complexes', ACS symposium 'Frontiers of Condensed Phase Theory and Simulation: A Tribute to Bruce J. Berne', Boston, Aug. 22-26, 2010, invited talk

Robert Silbey: 'Coherent Forster energy transfer in light-harvesting complexes', Solvay conference, Belgium, Oct, 2010, invited talk

Jianshu Cao: 'Signatures of quantum coherence in vibrational dynamics and energy transfer', Pacifichem symposium 'Coherence and its control in condensed phases', Hawaii, Dec. 15-17, 2010, invited talk

Jianshu Cao: 'Optimization of energy transfer processes in photosynthetic systems', Pacifichem symposium 'Theory of excited states structures and dynamics', Hawaii, Dec. 15-17, 2010, invited talk

Jianshu Cao: 'Generic models of single molecule kinetics and generalized MM equation', Telluride workshop, Telluride, June 26, 2011, invited talk

Jianshu Cao: 'Optimization of energy transfer processes in photosynthetic systems', Telluride workshop, July 4-10, 2011, invited talk
Jianshu Cao: 'Optimization of energy transfer processes in photosynthetic systems'. Field Institute, Toronto, July-Aug. 2011, invited talk

Jianshu Cao: 'Optimization of energy transfer processes in photosynthetic systems'. Complex system workshop, Dresden, November 2011, invited talk

Jianshu Cao: 'Statistical analysis of single molecule measurements'. APS, Boston, Feb. 2012, invited talk

Jianshu Cao: 'Optimization of energy transfer processes in photosynthetic systems'. ACS symposium, San Diego, March 2012, invited talk

Jianshu Cao: 'Optimization of energy transfer processes in photosynthetic systems'. Photosynthetic conference, NTU, Singapore, March 2012, invited talk

Jianshu Cao: 'Optimization of energy transfer processes in photosynthetic systems'. Beijing Normal University, June 2012, invited talk

Jianshu Cao: 'Optimization of energy transfer processes in photosynthetic systems'. USTC, June 2012, invited talk

Jianshu Cao: 'Statistical analysis of single molecule measurements'. Institute of Theoretical Physics, June 2012, invited talk

Jianshu Cao : 'Optimal Energy Transfer in Photosynthetic Systems', Dec. 2012, Hong Kong, invited talk

Jianshu Cao: ' Statistical Analysis of Single Molecule Measurements', Jan. 2013, Gordon Conference, invited talk

Jianshu Cao: 'Statistical Analysis of Single Molecule Measurement', March 2013, Telluride Workshop on Membranes, invited talk

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper	
12/18/2012	9.00	Wei Zhao , Justin Dauwels , Jacquin Niles , Jianshu Cao. Deconvolution of Microarray Data Predicts Transcriptionally Regulated Protein Kinases of Plasmodium falciparum, BIBM '11 Proceedings of the 2011 IEEE International Conference on Bioinformatics and Biomedicine. , . : ,

TOTAL: **1**

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received		Paper
01/26/2015	28.00	C. Chuang, J. Knoester, J. Cao. Scaling Relations and Optimization of Excitonic Energy Transfer Rates between One-Dimensional Molecular Aggregates, J. Phys. B: At. Mol. Opt. Phys. (03 2014)
11/08/2011	5.00	Jianlan Wu, Fan Liu, Jian Ma, Robert J. Silbey, Jianshu Cao. Efficient Energy Transfer in Light-Harvesting Systems, II:Quantum-Classical Comparison, Flux Network, and RobustnessAnalysis, Journal of Physical Chemistry (09 2011)
11/08/2011	6.00	Eric N. Zimanyi, Robert J. Silbey. Theoretical Description of Quantum Effects in Multichromophoric Aggregates, Royal Society (11 2011)
12/18/2012	7.00	A. K. Efremov, A. Li, J. Cao, X. Xu, M. Dao, C.T. Lim. Flow-based adhesion assay to study malaria red blood cell cytoadhesion, Biophysical Journal (12 2012)
TOTAL:		**4**

Number of Manuscripts:

Books

Received		Book
01/26/2015	4.00	Jianshu Cao, Jianlan Wu. GENERALIZED MICHAELIS–MENTENEQUATION FOR CONFORMATION-MODULATEDMONOMERIC ENZYMES, New Jersey, USA: John Wiley & Sons, (11 2011)
TOTAL:		**1**

Received	Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

J. Cao SMART Chair Professor at MIT
J. Cao Chair Visiting Professorship at Xiamen Univerity

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Zimanyi, Eric	0.16	
FTE Equivalent:	**0.16**	
Total Number:	**1**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Wu, Jianlan	0.50
FTE Equivalent:	**0.50**
Total Number:	**1**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Silbey, Robert J.	0.00	
Cao, Jianshu	0.10	No
FTE Equivalent:	**0.10**	
Total Number:	**2**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	0.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:.....	0.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:.....	0.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):.....	0.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:.....	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:	0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME PERCENT_SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

a) Generalized Michaelis-Menten equation and detailed balance

Enzyme catalysis is the most important chemical reactions in biology, and is the key step of many biochemical processes. The Michaelis-Menten mechanism (MM) has been the foundation for studying the steady-state kinetic behavior of enzymatic reactions. Recent single molecule experiments demonstrate that enzymatic reactions in a closed conformational environment follow the hyperbolic substrate dependence while many others deviate from this simple functional form. What can we say about an enzymatic reaction if the MM equation fails to describe its turnover rate? In a series of papers, we established the detailed balance (DB) as the sufficient condition for the MM form of enzymatic turnover rates and derived a non-equilibrium functional form of substrate-dependence in terms of unbalanced conformational currents.

Enzymatic reactions in biochemistry are far more complex than the celebrated MM scheme, but the observed turnover rate often obeys the hyperbolic dependence on the substrate concentration, a relation established almost a century ago for the simple MM mechanism. Recent single molecule studies of enzymatic reactions reveal that proteins fluctuate over a wide range of time scales, but turnover reactions of fluctuating enzymes are often found to obey the MM relation, which was originally derived for enzymes with a unique conformation. To resolve the longstanding problem, we apply the flux balance method to predict the functional form of the substrate dependence in the mean turnover time of complex enzymatic reactions and identify detailed balance (i.e. the lack of unbalanced conformational current) as a sufficient condition for the MM equation to describe the substrate concentration dependence of the turnover rate in an enzymatic network, thus establishing a connection to a fundamental property of non-equilibrium thermodynamics.

When the DB condition for the conformational states is violated, the MM functional form will break down, and the turnover rate will depend on the unbalanced current. Though explicit rate expressions are difficult to obtain, we established a functional form for the mean turnover time as MM terms plus non-MM correction terms arising from the presence of the non-equilibrium current in the cyclic loop. In fact, we can rigorously prove the one-to-one correspondence between the unbalanced currents and the independent hyperbolic terms and use this result to demonstrate a broad range of cooperative behaviors in non-equilibrium enzymes. Using this generalized MM rate expression, we were able to establish a phase diagram of different kinetic behaviors in enzyme networks, including positive cooperativity, substrate inhibition, bi-stability, and oscillations. This finding helps analyze recent single molecule studies of enzymatic networks and can be applied to other external variables, such as force-dependence in molecular motors and voltage-dependence in ion channels.

A major part of work has been published in a JPC special issue and in “Advances in Chemical Physics on Single Molecule Biophysics: Experiments and Theories”, a volume in the Advances in Chemical Physics series published by John Wiley publishers. Two more manuscripts are now ready for submission: one on the study of detailed balance violation, and the other on the general functional form of substrate dependence in reversible enzymatic reactions.

b) Counting statistics of single molecule/cell measurements

Fluctuations in reactivity of biological molecules are ubiquitous, and their effects on single molecule reaction trajectories become observable with the advent of modern single molecule experimental techniques. The emergent challenge in this field is to extract robust quantitative information from the noisy time series of single molecule reaction systems. In this project, we focus on a universal kinetic transition in reaction event counting statistics. By analyzing the Poisson indicator in the reaction event counting statistics, one can obtain quantitative information about the magnitude and the relaxation dynamics of reactivity fluctuations of biopolymer molecules without presuming a particular model for the conformational dynamics and reaction rate of a biopolymer.

Related to single molecule measurements, the single cell essay technique poses similar challenges in data analysis and defines a new area of statistical study. Specifically, the single cell microarray measurement collect large amount of data on protein expression, which is regulated by protein kinases of Plasmodium falciparum. We have developed a theoretical formulation to de-convolute and synchronize microarray data for better characterization of underlying genetic control involved in the malaria infection cycle.

Since the last report in 2011, this project has become a major direction in my group. Two more papers have since been published on single cell counting statistics. In 2013, we published a JPC paper jointly with a Los Alamos group on ‘universality of Poisson indicator and Fano factor of transport event statistics’. This paper will be followed by another manuscript on the generic scheme for enzymatic reactions. In these two papers, we systematically examine the functional form of substrate dependence.

c) Joint theoretical-experimental study of cytoadhesion and protein-receptor binding kinetics

The project is a part of the recent efforts in my group to develop a joint theoretical-experimental program in biophysics, including cell mechanics and adhesion. Cell adhesion plays a very important role in multi-cellular organisms, helping to maintain their integrity and homeostasis. This complex process involves many different types of adhesion proteins, and the synergetic behavior of these proteins during cell adhesion has been frequently observed in experiments. A well-known example is the cooperation of rolling and stationary adhesion proteins during the leukocytes extravasation. Despite the fact that such cooperation is vital for proper functioning of the immune response, its origin is still insufficiently understood. In this study, we constructed a simple analytic model for the interaction between leukocytes and blood vessel walls in shear flow and predict the bistability of cell adhesion. This bistabilty results from the competition between two kinetic processes in the cell-wall contact area – bonds formation and rupture. The theoretical model shows how physicochemical properties of adhesion proteins influence the adhesion bistability. Based on these results, we propose an explanation of the synergy between rolling and stationary adhesion proteins for effective cell adherence to the blood vessel wall in shear flow and provide possible interpretations of several cytoadhesion experiments.
The theoretical model on cell-adhesion was published in Biophysical Journal, and a joint theory-experiment manuscript was published in PLOS One. Currently, our effort is directed to the detailed study of the binding kinetics of cell-substrates, relating cytoadhesion to protein-receptor interaction. This effort leads to another manuscript under consideration in Biophysical Journal.

d) Coherent energy transfer in photosynthetic light-harvesting systems

In photosynthesis, excitation energy is transferred from pigments of the antenna to the reaction centers with remarkable efficiency. Recent experiments reveal that photosynthetic systems and their surrounding protein environments interact coherently to optimize transfer pathways and maximize efficiency. The high efficiency in natural systems has inspired scientists to design artificial systems for efficient conversion of solar energy into useful energy forms. These experimental results have motivated two theoretical questions: how to optimize the efficiency of energy transfer systems in dissipative environments and how to understand the optimization conditions in terms of network kinetics. In several recent manuscripts, we developed two theoretical approaches to address these questions: generic mechanism of optimal energy transfer and systematic expansion for mapping exciton dynamics to network kinetics.

The optimization of excitation energy transfer depends on initial preparation, static disorder, and the type of dynamic noise. To unify these different physical conditions into a single conceptual framework, we introduced the concept of orthogonal subspace, which is the part of exciton space that is decoupled from the trap state. In the coherent regime, the energy transfer from an orthogonal exciton subspace is prohibited and needs assistance of dynamic and static disorders. In the incoherent regime, excitation energy can be localized due to the dissipative effect from the surrounding environment. The competition between these two mechanisms thus leads to an optimization at an intermediate level of noise. The orthogonal subspace is a general concept for understanding optimal efficiency and can be found in systems with topological symmetry, limited quantum coherent strength, and large system size.

To interpret the analytical solutions for multi-level systems and the numerical solutions for realistic photosynthetic systems, we constructed a systematic expansion to map exciton dynamics to more intuitive network kinetics. The expansion defines an effective hopping rate as the leading order picture and non-local kinetic couplings as the quantum correction, leading to a rigorous separation of thermal hopping and coherent tunneling, and is a useful tool for visualizing pathway connectivity and interference in quantum networks. The mapping procedure allows us to apply the analytical tools developed for chemical networks to study photosynthetic energy transfer. We are currently working on a general kinetic expansion of quantum dissipation, which turns out to be equivalent to a generalization of NIBA (non-interacting blip approximation) for the spin-boson model to NICA (non-interacting cluster approximation) for multi-level exciton systems.

Late Professor Silbey was a leader in this research direction. Together, we published over 10 papers on this subject, including papers on PRL, Nature Communications, PNAS, and JPC letters. Also, we contributed to chapters in the recent book: ‘Quantum Effects in Biological Systems’. This project was sponsored jointly by this ARO grant (joint), NSF grant (individual), and a DARPA grant (joint).

Technology Transfer